DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer.

Supplementary Material Available: Tables of data collection parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (9 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Preparation and Study of the Fe_2^+–Benzyne Ion in the Gas Phase

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Received May 2, 1989

Previous studies have indicated that transition-metal dinuclear ions have reactivities very different from those of their constituent monoatomic ionic species.[1,2] One way to compare this is to study their reactivities with saturated hydrocarbons. For example, while Co^+ and Fe^+ are both very reactive with small alkanes, their dinuclear cluster ions Fe_2^+, Co_2^+, and $CoFe^+$ are unreactive.[3,4] Interestingly, the coordination of a seemingly very simple ligand can alter this reactivity completely. A study by Freas and Ridge indicated that Co_2CO^+ is reactive with small alkanes, in contrast to the inertness of the bare dinuclear species, and they explained this enhanced reactivity in terms of polarization induced by the carbonyl ligand.[4] However, more extensive study of the reactivities of dinuclear cluster ions and the effect of added ligands is necessary before the underlying factors governing the reactivity can be assessed in a systematic manner. Here we report on the preparation and the reactivity of the Fe_2^+–benzyne ion in the gas phase.

The study of transition-metal benzyne complexes is interesting because the transition-metal center greatly stabilizes the highly reactive benzyne ligand. Benzyne itself is very useful synthetically yet difficult to isolate and characterize because of its high degree of unsaturation.[5,6] A coordinatively unsaturated transition-metal benzyne complex is especially interesting because the metal center can potentially open up a wide variety of reaction channels by virtue of its oxidative addition ability, with the benzyne ligand then seeking whatever pathway available to satisfy its high degree of unsaturation. Our recent studies on the chemistry of Fe^+–benzyne with small alkanes and alkenes provide many examples of this reaction pattern, with Fe^+ acting as the reaction initiation center via its ability to oxidatively add into C–C and/or C–H bonds.[7,8]

All experiments in this study were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer previously described in detail.[9] The laser desorption method for generating gas-phase transition-metal ion species, the collision-induced dissociation (CID) experiment, and the pulsed-valve technique to manipulate gas-phase reagents have all been described previously in detail.[10-12]

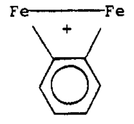
Table I. Reactions of $Fe_2C_6H_4^+$ with Alkanes

alkane	product	rel intens, %
methane	no reacn	
ethane	$Fe_2C_6H_6^+ + C_2H_4$	85
	$Fe_2C_8H_8^+ + H_2$	15
propane	$Fe_2C_6H_6^+ + C_3H_6$	84
	$Fe_2C_9H_8^+ + 2H_2$	6
	$Fe_2C_9H_{10}^+ + H_2$	10
n-butane	$Fe_2C_6H_6^+ + C_4H_8$	87
	$Fe_2C_{10}H_{10}^+ + 2H_2$	13
neopentane	$Fe_2C_7H_8^+ + C_4H_8$	100

The $Fe_2C_6H_4^+$ ion is prepared in the following sequence. Laser-generated Fe^+ first reacts with pulsed-in chlorobenzene to form $FeC_6H_4^+$,[13] which is then isolated by swept double-resonance ejections[14] and reacted with $Fe(CO)_5$ pulsed in through a second pulsed valve. The product ion $Fe_2(C_6H_4)(CO)_3^+$ is isolated and then undergoes CID at 44 eV in background argon, stripping the carbonyls away consecutively to give $Fe_2C_6H_4^+$, which is then isolated, and its reactions with other species are studied. An alternative pathway would be to first prepare Fe_2^+ by CID on $Fe_2(CO)_3^+$, which is in turn prepared from the reaction of Fe^+ with $Fe(CO)_5$. However, no $Fe_2C_6H_4^+$ is formed from the reaction of Fe_2^+ with chlorobenzene. Instead, it gives the condensation product $Fe_2C_6H_5Cl^+$ exclusively, which reacts further to give the secondary products $FeC_{12}H_{10}^+$, presumed to be Fe^+–biphenyl, and $FeCl_2$. This provides another example of the dramatic change in reactivity upon going from Fe^+ to Fe_2^+.

Unfortunately, the limited number of rf excitation pulses available on our instrument prevented further isolation and structural studies on the product ions, such as CID experiments. However, comparison of the chemistry observed here with that of Fe^+–benzyne could still provide some interesting insights into certain mechanistic aspects.

Previous studies on dinuclear transition-metal benzyne complexes in solution suggest a bridging benzyne ligand between the two metal centers.[15] Such a structure for Fe_2^+–benzyne is shown in I. CID of $Fe_2C_6H_4^+$ at 13 eV yields $FeC_6H_4^+$ exclusively. As CID energy increases, both $FeC_6H_4^+$ and Fe^+ are observed, with the latter accounting for ~15% of the fragment ions at 41 eV. These results, coupled with the absence of any Fe_2^+ fragment, are consistent with $D°(Fe^+–C_6H_4) \geq D°(Fe^+–Fe)$, previously reported to be 76 ± 10[7] and 62 ± 5 kcal/mol,[16] respectively. CID at a collision energy of 13 eV of a closely related yet less symmetrical species, $CoFeC_6H_4^+$, prepared by the above sequence from the reaction of $CoC_6H_4^+$ with $Fe(CO)_5$, gives ~65% $CoC_6H_4^+$ and ~35% $FeC_6H_4^+$, at least consistent with the bridging structure.



I

Previous studies have shown that $FeC_6H_4^+$ reacts sequentially with chlorobenzene to form a series of polymerization product ions consisting of iron polyphenylene and uncomplexed polyphenylene ions up to hexaphenylene.[7,13,17] In contrast, $Fe_2C_6H_4^+$ reacts with chlorobenzene by cleavage of the cluster ion, yielding $FeC_{12}H_9^+$ exclusively, with no further reactions observed. One

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(1) For a review on monoatomic transition-metal ion chemistry, see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J. Ed.; Wiley-Interscience: New York, 1986; Vol. 34; p 628 and references therein.

(2) Examples: Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 1581. Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 6222. Tews, E. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 4433.

(3) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

(4) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.

(5) Examples: McLain, S. J.; Schrock, R. B.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. Goemz-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1682.

(6) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967.

(7) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 2387.

(8) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

(9) Cody, R. B.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

(10) Examples: Freiser, B. S. *Talanta* **1985**, *32*, 697. Freiser, B. S. *Chemtracts* **1989**, *1*, 65.

(11) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436.

(12) Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

(13) Dietz, T. G.; Chatellier, D. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 4905.

(14) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413.

(15) Dobson, J. E.; Miller, R. G.; Wiggen, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 554.

(16) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 3537.

(17) Bjarnason, A.; Taylor, J. W. *Organometallics* **1989**, *8*, 2020.

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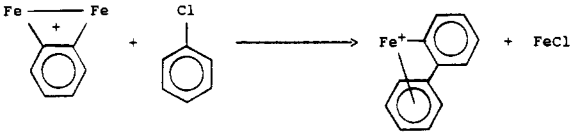
possible mechanism for this reaction would be insertion of the dinuclear metal center into the Cl–phenyl bond, followed by migratory insertion of the phenyl group into the benzyne ligand. Finally, cleavage of the Fe–Fe bond and subsequent FeCl elimination give the (η^7-biphenyl-2-yl)iron product ion, as shown in reaction 1.



(1)

As is mentioned above, small alkanes are a good basis to compare the reactivity of small gas-phase transition-metal ion species, and thus, the chemistry of $Fe_2C_6H_4^+$ with small alkanes was studied. As shown in Table I, all of the alkanes studied, with the exception of methane, are reactive with the Fe_2^+–benzyne ion. Unlike the case of the reaction with chlorobenzene, the dinuclear metallic center Fe_2 remains intact in all of the reactions. For ethane, propane, and *n*-butane, hydrogenation of the benzyne ligand to form $Fe_2C_6H_6^+$, presumably Fe_2^+–benzene, is by far the predominant pathway.

The hydrogenation of benzyne by an alkane to form benzene and the corresponding alkene is significantly exothermic, for example, ~48 kcal/mol for ethane.[18,19] Surprisingly, reports of such reactivity between neutral benzyne and an alkane are scarce, with the only exception being data for cyclohexane.[6] However, this does suggest the possibility that the reactions observed in Table I might occur directly between the alkane species and the benzyne ligand itself. In the case of Fe^+–benzyne, evidence was presented suggesting that the observed reactivity is initiated by the metal ion center.[7] While both Fe_2^+–benzyne and Fe^+–benzyne follow the same reactivity pattern with these small alkanes, i.e. being reactive with all of the alkanes except methane, somewhat different product ions and ion distributions are observed. For example, there is no hydrogenation product for the reaction of Fe^+–benzyne with ethane.[7] Instead, $FeC_8H_8^+$, determined to be Fe^+–benzocyclobutene, is formed, exclusively. For the reaction of Fe^+–benzyne with propane and *n*-butane, additional products, such as Fe^+–toluene and Fe^+–styrene, are observed. The change of the overall reaction pattern with the specific metal ion center involved, including the type of product ions and distributions, thus reenforces the argument that the reactions observed in Table I are not due to the benzyne ligand itself, but instead are initiated by the oxidative addition ability of the metal center.

As is the case for Fe^+–benzyne, the hydrogenation of $Fe_2C_6H_4^+$ to form $Fe_2C_6H_6^+$ can be simply explained by initial insertion of the dinuclear metal ion center into a C–H bond, followed by hydrogen migration to the benzyne ligand to form an intermediate Fe_2^+–(alkyl)(phenyl) ion. A β-hydrogen atom on the alkyl group is subsequently abstracted by the metal center and it couples with the phenyl group to form an Fe_2^+–(alkene)(benzene) ion. The exothermicity of this process is enough to eliminate the more weakly bound alkene ligand to complete the reaction. The lack of the hydrogenation product ion for neopentane supports the above mechanism, indicating that the hydrogenation process requires that the alkane have hydrogen atoms on neighboring carbon atoms. To further probe this mechanism, the reaction with propane-*2,2-d*$_2$ was studied. Approximately 90% $Fe_2C_6H_5D^+$ was observed for the hydrogenation product ion, indicating the predominance of the simple 1,2-hydrogenation process as expected. Although the presence of ~10% $Fe_2C_6H_6^+$ may suggest an additional 1,3-hydrogenation process, this product could also arise due to a reversible step during the β-hydrogen abstraction step causing scrambling.

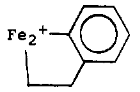
In the case of neopentane, a β-methyl abstraction occurs following initial C–H insertion because of the lack of a β-hydrogen atom, resulting in Fe_2^+–toluene formation. Alternatively, initial C–C bond insertion with ensuing β-hydrogen abstraction would lead to the same product ion. However, the methanation product ion should also have been observed if the latter pathway were adopted for propane and *n*-butane. The predominant formation of the hydrogenation product ion and the lack of $Fe_2C_7H_8^+$, therefore, both point to the preference of C–H insertion over C–C bond insertion by the dinuclear metal center, suggesting that the reaction with neopentane more likely occurs by initial C–H insertion.

When $Fe_2C_6H_4^+$ reacts with ethylene, cleavage of the cluster center and appearance of the bare dinuclear ion are both observed (reactions 2 and 3). The simultaneous formation of both Fe_2^+

$$Fe_2C_6H_4^+ + C_2H_4 \rightarrow Fe_2^+ + C_8H_8 \quad 55\% \qquad (2)$$

$$\rightarrow FeC_8H_8^+ + Fe \quad 45\% \qquad (3)$$

and $FeC_8H_8^+$ suggests that $D°(Fe_2^+–C_8H_8)$ is similar to $D°(FeC_8H_8^+–Fe)$ and that $D°(Fe^+–C_8H_8)$ is similar to $D°(Fe^+–Fe)$ = 62 ± 5 kcal/mol.[20] In the reaction of Fe^+–benzyne with ethylene, Fe^+ and $FeC_8H_8^+$ are also observed, with the latter having an Fe^+–benzocyclobutene structure.[8] Considering the similarity with the Fe^+–benzyne reaction with ethylene, it is highly likely that the ion in reaction 3 has the analogous structure. The reactions may occur by the migratory insertion of the ethylene ligand between the metal center and the benzyne ligand to form an intermediate benzometallacyclopentene, structure II, which then rearranges to Fe_2^+–benzocyclobutene. The energy gained from the process to form the benzocyclobutene ligand, once again, is high enough to induce the competitive elimination of Fe and C_8H_8. An intermediate such as structure II is stable in solution and has been isolated for several transition-metal benzyne complexes.[21] However, the possibility of simple coupling between the benzyne ligand and the incoming ethylene cannot be ruled out. Assuming the benzocyclobutene structure and given ΔH_f(benzyne) = 100 ± 5 kcal/mol[18] and ΔH_f(benzocyclobutene) = 48 ± 1 kcal/mol,[18] the appearance of Fe_2^+ in reaction 2 suggests $D°(Fe_2^+\text{–benzyne}) \leq 73 \pm 6$ kcal/mol. This upper limit can be compared to $D°(Fe^+$–benzyne) = 76 ± 10 kcal/mol[7] and $D°(Sc^+$–benzyne) = 97 ± 7 kcal/mol.[22] One uncertainty lies in the heat of formation value for benzyne. It was earlier reported as 118 kcal/mol, which would have given a bracket of $D°(Fe_2^+$–benzyne) ≤ 86 kcal/mol.[19] Finally, for comparison, $D°(Fe^+$–benzene) = 55 ± 5 kcal/mol[23] and $D°(Fe_2^+$–benzene) ≃ 50 kcal/mol.[24]



II

A surprising variety of product ions are observed from the reaction of Fe_2^+–benzyne with propene (reactions 4–12). In

$$Fe_2C_6H_4^+ + C_3H_6 \rightarrow FeC_6H_6^+ + (FeC_3H_4) \quad 2\% \qquad (4)$$

$$\rightarrow FeC_7H_8^+ + (FeC_2H_2) \quad 8\% \qquad (5)$$

$$\rightarrow FeC_9H_8^+ + (FeH_2) \quad 8\% \qquad (6)$$

$$\rightarrow FeC_9H_{10}^+ + Fe \quad 25\% \qquad (7)$$

$$\rightarrow Fe_2^+ + C_9H_{10} \quad 5\% \qquad (8)$$

$$\rightarrow Fe_2C_3H_4^+ + C_6H_6 \quad 13\% \qquad (9)$$

$$\rightarrow Fe_2C_6H_6^+ + C_3H_4 \quad 13\% \qquad (10)$$

$$\rightarrow Fe_2C_7H_8^+ + C_2H_2 \quad 7\% \qquad (11)$$

$$\rightarrow Fe_2C_9H_8^+ + H_2 \quad 19\% \qquad (12)$$

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(18) Moini, M.; Leroi, G. F. *J. Phys. Chem.* **1986**, *90*, 4002.

(19) Lias, G. L.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*.

(20) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 3537.

(21) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(22) Huang, Y.; Sun, D.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

(23) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

(24) Lech, L. M.; Freiser, B. S. Ph.D. Thesis, Purdue University, 1988.

contrast, $FeC_7H_8^+$ is the only product ion formed from the reaction of Fe^+–benzyne. Once again, the dramatic change of reactivity upon going from $FeC_6H_4^+$ to $Fe_2C_6H_4^+$ indicates the important role of the metal center and suggests, therefore, that the reaction is probably initiated by the metal center, and is not simply between the ligands themselves. The type of product ions observed suggests that the cluster center inserts into both C–C and C–H bonds of propene.

In conclusion, the reactivity of Fe_2^+–benzyne is much different from that of Fe_2^+ and Fe^+–benzyne. The enhanced reactivity toward alkanes of $Fe_2C_6H_4^+$ with respect to that of bare Fe_2^+ probably arises due to two effects. First, in analogy to the Co_2CO^+ case discussed above, the ligand polarizes or in some way changes the electronic structure of the metal center to permit oxidative addition. Second, the coordination of the highly unsaturated benzyne ligand provides a very efficient pathway for further steps following initial metal center oxidative insertion, with the high exothermicity gained from partially saturating the C–C triple bond of the benzyne ligand to a double bond providing a significant driving force. Unlike Fe^+–benzyne, its dinuclear metal counterpart does not polymerize chlorobenzene around the metal center. In the reaction with small alkanes, the dinuclear benzyne complex ion seems to prefer C–H insertion over C–C insertion, resulting in the predominant formation of the hydrogenation product ion, Fe_2^+–benzene, while Fe^+–benzyne generates significantly more product ions corresponding to C–C bond insertion.

Acknowledgment is made to the Division of Chemical Sciences, Office of Basic Sciences, U.S. Department of Energy (Grant DE-FG02-87ER13766), for supporting this research and to the National Science Foundation (Grant CHE-8612234) for continued support of the FTMS.

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X-ray Study of Ta(CHCMe$_3$)(S-2,4,6-C$_6$H$_2$-i-Pr$_3$)$_3$(SEt$_2$) Suggests Why It Is Inactive for Metathesis of Ordinary Olefins

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Received July 11, 1989

Tantalum alkylidene complexes of the type $Ta(CHCMe_3)(DIPP)_3(THF)$ (DIPP = O-2,6-C_6H_3-i-Pr_2) will react readily with terminal olefins or ethylene to give "base-free" tantalacyclobutane complexes (e.g., with styrene to give Ta[CH(Ph)CH(t-Bu)-CH_2](DIPP)$_3$) or new alkylidene complexes (e.g., with vinyltrimethylsilane to give $Ta(CHSiMe_3)(DIPP)_3(THF)$).[1] They are quite active catalysts (several hundred turnovers) for the metathesis of ordinary internal olefins such as *cis*-2-pentene, although longevity is limited by instability of one or more intermediates, most likely alkylidene complexes in which a β proton is present. (No example has yet been observed.) In contrast, $Ta(CHCMe_3)(TIPT)_3(THF)$ (TIPT = S-2,4,6-C_6H_2-i-Pr_3) does not react with ordinary olefins and will not metathesize them. $Ta(CHCMe_3)(TIPT)_3(py)$ *will* react with norbornene to give *stable* Ta{[CH(C_5H_8)CH]$_x$CHCMe$_3$}(TIPT)$_3$(py), in which a β proton is present. Base-free (five-coordinate) tantalacyclobutane complexes made from norbornene are observed when DIPP ligands are present, but not when TIPT ligands are present.

We speculated that the structures of Ta(CHR)(TIPT)$_3$(base) complexes differ fundamentally from those of the type Ta(CHR)(DIPP)$_3$(base) and that this is at least part of the reason for the strikingly different chemistry of the two types of complexes. A structure of a complex of the latter type, a vinylalkylidene complex, Ta[C(Me)C(Me)CHCMe$_3$](DIPP)$_3$(py), prepared by adding pyridine to a metallacyclobutene complex prepared from $Ta(CHCMe_3)(DIPP)_3(THF)$ and 2-butyne, showed it to be approximately a trigonal bipyramid containing an η^1-vinylalkylidene ligand in an equatorial position and a pyridine ligand in an axial position.[2] One can propose that the axial pyridine ligand in Ta[C(Me)C(Me)CHCMe$_3$](DIPP)$_3$(py) occupies the same position that an incoming olefin would occupy and that formation of an "axial/equatorial" tantalacyclobutane ring could take place readily. We have now prepared a suitably crystalline $Ta(CHCMe_3)(TIPT)_3$(base) derivative (base = diethyl sulfide) and have determined its structure. The structure is, in fact, significantly different from that of the DIPP relative and goes a long way toward explaining the different catalytic behavior of the TIPT versus the DIPP complexes.

Experimental Section

Preparation of $Ta(CHCMe_3)(TIPT)_3(SEt_2)$. Diethyl sulfide (94 μL, 0.87 mmol) was added via syringe to a stirring solution of $Ta(CHCMe_3)(TIPT)_3(THF)$[1] (0.300 g, 0.29 mmol) in ether (10 mL) at room temperature. The color of the solution remained orange. After 15 min the solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The resulting orange-red solid was dissolved in pentane, and the solution was cooled to −30 °C to give large orange crystals (0.203 g, 66%). ^{1}H NMR: δ 7.15 (s, C_m), 3.93 (septet, 6, ortho CHMe$_2$), 2.83 (para CHMe$_2$), 2.47 (q, 4, CH$_3$CH_2S), 1.36 (d, 36, ortho CHMe_2), 1.25 (d, 18, para CHMe_2), 1.02 (t, 6, CH_2CH$_2$S), 0.83 (s, 9, CHCMe_3). ^{13}C NMR: δ 262 (broad, J_{CH} unresolved, CHCMe$_3$), 151.1, 149.1, and 134.2 (C_{ipso}, C_o, and C_p), 121.7 (C_m), 48.0 (CHCMe$_3$), 34.6 (para CHMe$_2$), 33.0 (ortho CHMe$_2$), 32.4 (CHCMe_3), 27.6 (broad t, CH$_3$$CH_2$S), 24.5 (para CH$Me_2$), 24.0 (ortho CH$Me_2$), 15.1 (CH$_3$$CH_2$S). (Routine multiplicities are not listed.) The alkylidene proton resonance is assumed to be found in the complex region around 4 ppm, as it is in the analogous pyridine adduct.[1] Ligand exchange leads to broadening of the resonance at 25 °C, and spectra were too complex at all temperatures to locate the resonance difinitively. The situation in the case of the THF adduct is analogous.[1] Elemental analyses were low for C, H, and S, we presume because of the lability of the diethyl sulfide ligand.

X-ray Study. A yellow plate of $Ta(CHCMe_3)(TIPT)_3(SEt_2)$ having approximate dimensions 0.150 × 0.350 × 0.350 mm was mounted on a glass fiber that was transferred to the diffractometer in a cold stream of dinitrogen. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $22.00° < 2\theta < 32.00°$, corresponded to a triclinic cell with dimensions a = 17.458 (3) Å, b = 19.109 (4) Å, c = 10.096 (2) Å, α = 90.77 (2)°, β = 102.41 (2)°, γ = 116.65 (1), V = 2917 (3) Å^3, and Z = 2. For a fw = 1047.48, the calculated density is 1.192 g/cm^3. The space group was determined to be $P\bar{1}$ (No. 2). Data were collected at a temperature of −70 ± 1 °C by using the ω-scan technique to a maximum 2θ value of 55.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26°. Scans of $(1.09 + 0.35 \tan\theta)°$ were made at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of two rescans), and the counts were accumulated to ensure good counting statistics. Stationary-background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

Of the 13 850 reflections collected, 13 410 were unique (R_{int} = 0.038); equivalent reflections were merged. The intensities of three representative reflections that were measured after every 197 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo Kα is 20.3 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.77 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by the Patterson method.[3] The non-hydrogen atoms were refined either anisotropically or isotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d_{C-H} = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the B_{equiv} values of the atoms to

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(1) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964.

(2) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.

(3) Walker, N.; Stuart, D. *Acta Crystal.* **1983**, *A39*, 158.